

AECD - 2426

UNITED STATES ATOMIC ENERGY COMMISSION

A HIGH TEMPERATURE PRECISION X-RAY CAMERA

Some Measurements of the Thermal Coefficients of Expansion of Beryllium

by

Paul Gordon

October 1, 1948

Massachusetts Institute of Technology

FILE COPY
Science and Technology Project
Library of Congress
DO BE RETURNED

This document is reproduced as a project report and is without editorial preparation. The manuscript has been submitted to The Journal of Applied Physics for possible publication.

DTIC QUALITY INSPECTED 2

Issuance of this document does not constitute authority for declassification of classified copies of the same or similar content and title and by the same author.

This document has been reproduced by direct photography from copy as submitted to this office

Technical Information Branch, Oak Ridge, Tennessee
AEC, Oak Ridge, Tenn., 2-18-49--850-A1873

Printed in U.S.A.

~~PRICE 15 CENTS~~

DISTRIBUTION STATEMENT A

Approved for public release;
Distribution Unlimited

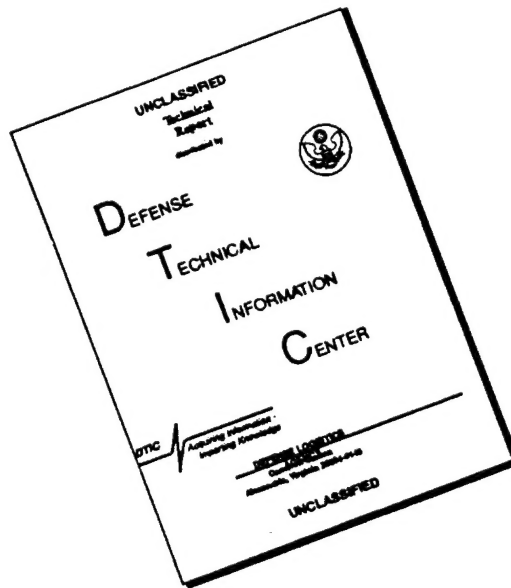
19961016 384

215290

48

MAR 15 1949

DISCLAIMER NOTICE



THIS DOCUMENT IS BEST QUALITY AVAILABLE. THE COPY FURNISHED TO DTIC CONTAINED A SIGNIFICANT NUMBER OF PAGES WHICH DO NOT REPRODUCE LEGIBLY.

AECD - 2426

A HIGH TEMPERATURE PRECISION X-RAY CAMERA

SOME MEASUREMENTS OF THE THERMAL COEFFICIENTS OF EXPANSION OF
BERYLLIUM

ABSTRACT

A high temperature precision x-ray camera has been designed and constructed by modification of the familiar back reflection symmetrical focussing type of camera. The camera, specimen and furnace are used within a vacuum chamber to avoid oxidation. The apparatus in its present form has been employed at temperatures up to 1000°C, but higher temperatures could be easily attained by making a few minor changes in the furnace materials.

The lattice parameters of beryllium have been measured up to 1000°C. The derived coefficients of thermal expansion, both linear and bulk, are presented as a function of temperature. In addition, the data present strong evidence that the hexagonal close packed form of beryllium which exists at room temperature is stable up to at least 1000°C, contrary to several reports in the literature.

A HIGH TEMPERATURE PRECISION X-RAY CAMERA

SOME MEASUREMENTS OF THE THERMAL COEFFICIENTS OF EXPANSION OF BERYLLIUM*

The desirability of accurately measuring the lattice parameters of beryllium at elevated temperatures has led to the design and construction of a high temperature precision x-ray camera. Some data on the thermal expansion of beryllium have been obtained and are presented in this paper along with a description of the camera.

I. Description of the Camera

The camera is basically a modification of the familiar back reflection symmetrical focussing design. The adaptation of this design to the needs of high temperature work is illustrated in the drawings of Figure 1 and the photograph of Figure 2. The rear segment of the camera which ordinarily holds the specimen was made removable. Thus, for room temperature measurements this segment can be easily attached by means of set screws and the camera used in the normal way. For high temperature measurements, the rear segment is removed to make room for the furnace. In this case the specimen is held in its proper position on the circumference along which the slit and film lie by means of an adjustable supporting arm extending out from a post at the top center of the camera. To the specimen end of this arm is attached a vertical circular disc (stainless steel) having its rear surface machined to the same radius ($2\frac{1}{2}$ ") as the camera. The

* This document is based on work performed on the Metallurgical Project, Massachusetts Institute of Technology under Contract No. W-7405-eng-175 for the Atomic Energy Commission.

disc is positioned so that its curved rear surface lies along the camera circle by pressing its flat front face against a spacer placed between the disc and the flat surfaces of the camera body exposed by the removal of the rear segment. As a result the specimen is in the proper position to satisfy the focussing conditions of the camera when it is held against the rear surface of the disc.

For reasons which will be given later, the beryllium specimen was made by pressing fine beryllium powder into one end of a longitudinal hole in a cylindrical beryllium holder, this end of the specimen holder being ground to fit the curved surface of the disc. The holder fits snugly into a hole in a cylindrical molybdenum rod (about 1" diam., 1" long) with the face of the specimen flush with the properly curved face of the molybdenum cylinder. The latter is fastened to the stainless steel disc by two stainless steel screws and thus serves to hold the specimen in position over a hole drilled through the disc to allow passage of the x-ray beam.

The specimen is heated by a small resistance furnace consisting of a platinum winding on a 1" diam. alundum core surrounded by a 1" layer of K-30 insulating brick, the whole being contained in a sheet metal cylinder. The transverse faces of the furnace are $\frac{1}{4}$ " transite. The furnace is, thus, a cylinder approximately $3\frac{1}{2}$ " in diameter and $1\frac{1}{2}$ " long with a tubular muffle of just the right size to enclose the molybdenum cylinder in which the specimen is held. The furnace is fixed in place by clamping it to the supporting arm described above.

In order to protect the specimen and the various heated parts from oxidation, the whole assembly consisting of the camera, specimen support, specimen and furnace is placed in a vacuum chamber (see photographs in Figures 3 and 4). The chamber is simply a length of 9" diam. copper

tubing with a brass plate brazed to the front end (facing the x-ray beam) and a second, removable brass plate held in place at the rear by wing nuts. A rubber gasket coated with Celvacene high vacuum grease insures a vacuum tight seal between this plate and the copper chamber. The bottom of the chamber is fitted with a grooved adapter so that it may be clamped to the track of the Picker x-ray diffraction unit used as the x-ray source. The x-ray beam enters the vacuum chamber through a beryllium window (thickness = 0.005") in the front brass plate.

Using a Welsh Duo-Seal forepump and a metal oil diffusion pump (Distillation Products) pressures as low as 5×10^{-6} mm. of Hg were obtainable with the furnace and specimen at room temperature. During high temperature runs, pressures of 10^{-5} mm. of Hg were obtained after time was allowed for the degassing of the heated parts. In order to minimize the degassing period and its associated oxidation, CO_2 rather than air was introduced into the vacuum chamber each time it had to be brought to atmospheric pressure.

The heat radiated by the furnace to the vacuum chamber walls and the camera is carried away by copper water-cooling coils. In the case of the chamber, these coils are soldered to the outside wall surfaces. The camera cooling coils are held tightly against the top and bottom camera surfaces by means of specially constructed clamps. The coils are connected to the water supply by rubber pressure tubing joined to short lengths of copper tubing, the latter being soldered through the vacuum chamber wall. In addition, a beryllium radiation shield (0.002" sheet Be) across the section of the camera facing the furnace serves to protect the photographic film in the camera against direct heat radiation from the furnace.

II. Specimen Preparation

The preparation of beryllium specimens suitable for back reflection x-ray measurements involves difficulties not encountered with heavier metals. With most metals a thin sprinkling of fine powder on a suitable backer, or a fine-grained solid piece with random grain orientation make satisfactory specimens. Because of the relatively high atomic numbers of such metals the x-rays penetrate only a very shallow surface layer of the specimen and an appreciable proportion of the x-ray energy is diffracted to the film. On the other hand, x-rays of the wave lengths used in diffraction work easily penetrate as much as 5-10 mm. of beryllium. This leads to several difficulties. First, it means that very little x-ray energy would be diffracted from a thin beryllium powder specimen and hence the exposure time would be prohibitively long. Second, although increasing the thickness of the specimen would shorten exposure time, the ultimate thickness to which one may go is limited by the necessity of meeting the focussing conditions of the camera. That is, for very thick specimens, the diffraction lines would tend to become broad, thus decreasing the accuracy of measurement, since the high penetrating power of the x-rays would result in diffraction not only from the surface, but from practically the full depth of the specimen. And third, the fact that a large portion of the X-radiation would be transmitted through even a very thick beryllium specimen means that anything behind the specimen would produce complicating diffraction lines and/or background intensity on the x-ray film. Thus, the space behind the specimen must be kept empty.

The most satisfactory beryllium specimen for use in a back reflection powder camera would be one made from a fine-grained solid piece having random grain orientation. In this case the maximum amount of metal for

a given specimen thickness could be placed in the path of the beam. However, the only relatively fine-grained beryllium available today is extruded material having a high degree of preferred orientation. The lack of randomness results in the loss of certain diffraction lines on the x-ray photograph. Consequently, the beryllium specimens for the present work were finally made by compressing very fine powder into the form of discs about .025" thick. Pressures of about 40-50000 psi produced a density in the discs of approximately 60 to 70% that of solid Be. The powder was pressed into one end of a hole in a cylindrical beryllium holder as shown in the sketch of Figure 5. A particle size of about 10 microns was used to obviate the necessity for rotating or translating the specimens. The cold working stresses incurred during the pressing were relieved by annealing the specimen for 1 hour at 600°C in vacuo.

III. Temperature Measurement and Control

Measurement of the temperature of the specimen proved to be the most troublesome part of the procedure for making a high temperature picture. Because a thermocouple could not be attached directly to the pressed powder specimen, its temperature was measured by welding a chromel-alumel couple to the front face of the beryllium holder as close to the specimen as possible (see Figure 5). It was found to be very important to bring the thermocouple wires to the point of measurement through the furnace in order to eliminate heat losses from the hot junction by conduction through the thermocouple wires themselves. Failure to take this precaution was capable of producing errors in temperature determination of as much as 50°C, even with the very thin wire used. It was recognized that an appreciable temperature difference might exist between the position of the hot junction and the central part of the specimen on which the

x-ray beam actually impinged. To minimize this difference two radiation shields of 0.002" Be sheet were placed across the furnace in front of the specimen and in contact with the heated stainless steel disc on the support arm. Under these conditions several calibration runs were made in an effort to measure the temperature difference between the hot junction and the center of the specimen. This was done by replacing the powder specimen with a solid, dummy specimen (in several cases molybdenum dummy specimens and molybdenum holders were used) spot-welding a second couple to the center of the front face of this dummy specimen, heating to various temperatures in vacuum and recording the difference in reading between the two couples. The difference was found to be less than 5°C for all temperatures up to 1000°C; an average correction as a function of temperature was obtained from the several calibration runs made and was applied to all subsequently measured temperatures*.

The thermocouples used were replaced for each new run, that is, each temperature recorded in the data (see Appendix) was registered with a fresh couple. This was done to eliminate the possible effects of contamination of the thermocouple wires, particularly by beryllium vapors. Test calibration of a once-used couple (used at high temperature) against a fresh one showed no significant difference in reading. All couples were made from the same batches of chromel and alumel wire, so that no appreciable relative error in temperature reading was introduced by the practice of using a new couple for each run.

*This correction, of course, could be rigorously applied only to solid specimens; it was felt, however, that this represented as close an approach to the actual temperature of the powder specimen as could be obtained, and that the errors still unaccounted for were second-order effects.

Temperature control was obtained with the use of a voltage stabilizer and a variac. Temperatures could usually be held to within 2-5°C in this way. Thus, the total temperature uncertainty for any run was seldom greater than about $\pm 3^\circ\text{C}$ (including that due to the uncertainty in the correction described above). It is believed, however, that the attaining of better temperature control would be advantageous in future work, since the largest part of the inaccuracies in the present measurement of parameter changes with temperature can be attributed to this uncertainty in the temperature of the specimen.

IV. X-Ray Technique

The back reflection symmetrical focussing camera is an absolute instrument capable of giving lattice constants to an accuracy of 0.005% or better. No standard substance of known parameter need be used. For cubic crystals, the systematic errors due to camera radius error, absorption in the specimen and film shrinkage may be eliminated by plotting the parameter calculated from individual diffraction lines against the function $\phi \tan (\phi/2)$ where $\phi = \pi - \frac{\Theta}{2}$ and Θ is the Bragg angle⁽¹⁾. Extrapolation to $\phi \tan (\frac{\phi}{2}) = 0$ gives the corrected value of the parameter. For non-cubic crystals, such as beryllium (HCP), the graphical extrapolation may not be used accurately, but an analytical method for extrapolating to eliminate the systematic errors has been developed by M. U. Cohen⁽¹⁾.

Cohen finds, as indicated above, that symmetrical focussing cameras have systematic errors in $\frac{\Delta^d}{d}$ (d = lattice spacing) that are proportional to $\phi \tan (\frac{\phi}{2})$ in the range $\sin^2 \Theta > 0.7$. Thus

$$(1) \frac{\Delta^d}{d} = D \phi \tan (\frac{\phi}{2})$$

(1) M. U. Cohen, Rev. Sci. Instruments, Vol. 6, p. 68, 1935
Vol. 7, p. 155, 1936; Z. Krist, Vol. 94, pp. 288, 306, 1936

By squaring Bragg's law and taking logs we have

$$(2) \quad 2 \log d = -\log \sin^2 \Theta + 2 \log \left(\frac{n\lambda}{2} \right)$$

Differentiating (2) and substituting the value of $\frac{\Delta d}{d}$ from (1) gives

$$\Delta \sin^2 \Theta = 2 D \left[\phi \tan \left(\frac{\phi}{2} \right) \right] \sin^2 \Theta$$

and since $\Theta = \frac{\pi}{2} - \frac{\phi}{2}$, and $\sin^2 \Theta = \cos^2 \frac{\phi}{2}$

$$\Delta \sin^2 \Theta = D \phi \sin \phi$$

Thus, the systematic errors lead to errors in the measured $\sin^2 \Theta$ values which are proportional to $\phi \sin \phi$. Adding this correction to the quadratic form for hexagonal crystals,

$$\sin^2 \Theta = A(h^2 + hk + k^2) + C(l^2) + D \phi \sin \phi$$

which may be written

$$\sin^2 \Theta = \alpha A + \gamma C + \delta D$$

where $A = \frac{\lambda^2}{3a_0^2}$, $C = \frac{\lambda^2}{4c_0^2}$

$$\alpha = h^2 + hk + k^2$$

$$\gamma = l^2$$

$$\delta = 5 \phi \sin \phi$$

$$D = \text{proportionality constant}$$

With a set of measured $\sin^2 \Theta$ values at hand for a given film, A and C may now be found by the method of least squares. The three normal equations are set up

$$\sum \alpha \sin^2 \Theta = A \sum \alpha^2 + C \sum \alpha \gamma + D \sum \alpha \delta$$

$$\sum \gamma \sin^2 \Theta = A \sum \alpha \gamma + C \sum \gamma^2 + D \sum \gamma \delta$$

$$\sum \delta \sin^2 \Theta = A \sum \alpha \delta + C \sum \gamma \delta + D \sum \delta^2$$

the summation being carried out over all the equations of the separate diffraction lines. Solution of the simultaneous equations yields the corrected values of A and C, and thus, of the lattice constants a_0 and c_0 . It will be found, however, that in most cases the solution of the simultaneous equations involves the loss of significant figures. The use of

a simple mathematical device circumvents this difficulty and in addition makes it unnecessary to carry an inconveniently large number of significant figures in the calculations. The three normal equations are replaced by another set in the following way: Values of the constants A and C are calculated from the best available approximations of the lattice parameters a_0 and c_0 . These values may be designated A_A and C_A , the subscript indicating "assumed". From A_A and C_A , assumed values of $(\sin^2 \Theta)_A$ can be obtained, neglecting the term $D \sin \Theta$ in the quadratic equation. Now, letting

$$\Delta A = A_A - A_E$$

$$\Delta C = C_A - C_E$$

$$\Delta D = D_A - D_E$$

$$\Delta \sin^2 \Theta = (\sin^2 \Theta)_A - (\sin^2 \Theta)_E = \nu$$

where the subscript (E) indicates the experimentally determined values, it will be seen that the new normal equation may be written

$$\xi \propto \nu = \Delta A \xi \alpha^2 + \Delta C \xi \alpha \gamma + \Delta D \xi \alpha \delta$$

$$\xi \gamma \nu = \Delta A \xi \alpha \gamma + \Delta C \xi \gamma^2 + \Delta D \xi \gamma \delta$$

$$\xi \delta \nu = \Delta A \xi \alpha \delta + \Delta C \xi \gamma \delta + \Delta D \xi \delta^2$$

Solution of these equations for ΔA and ΔC now yields values of A_E and C_E from the defining relationships above. Since ΔA and ΔC are small corrections to be applied to A_A and C_A to obtain the experimental values, only a few significant figures need be carried in the calculations.

The accuracy of the mathematical extrapolation described above is naturally the better the greater the number of diffraction lines with $\sin^2 \Theta > 0.7$ appearing on the film. In the present work both Co and Fe radiations were employed for each photogram produced in order to obtain a sufficient number of diffraction lines. Making use of both the K_α and K_β wave lengths (see Table I) from these two targets, 13 usable diffraction

lines appeared on the film at specimen temperatures near room temperature, while at the higher temperature up to 16 lines were produced. Operating at 40 kv and 10 milliamps, the exposures required for satisfactory photographs were of the order of 1-2 hours for each target (2-4 hrs. total for each film).

Table I.

Wave Lengths of Radiations Used

| Radiation | Wave Length, k X Units |
|---------------|------------------------|
| Fe α_1 | 1.932076 |
| Fe α_2 | 1.936012 |
| Fe β | 1.753015 |
| Co α_1 | 1.78529 |
| Co α_2 | 1.78919 |
| Co β | 1.61744 |

V. Lattice Dimensions of Beryllium as a Function of Temperature

The beryllium used for the present measurements was obtained in the form of -325 mesh powder from the Brush Beryllium Company. Powder particles having a size of about 10 microns or less were separated from the remainder in an infrasizer. This very fine powder was then used to make the x-ray specimens. The quantities of impurities present in the separated powder are listed in Table II. The possible effect of these impurities on the lattice constants of beryllium is considered to be very small.

Table II.

Major Impurities in the Beryllium Powder

| Element | Wgt. % | At. % |
|---------|--------|--------|
| Fe | 0.084 | 0.016 |
| Al | 0.280 | 0.104 |
| Si | 0.141 | 0.047 |
| Mg | 0.580 | 0.23 |
| C | 0.06 | 0.05 |
| Ca | 0.07 | 0.02 |
| Cu | <0.01 | <0.002 |
| Mn | 0.04 | 0.007 |
| Ni | 0.01 | 0.002 |

It has been shown in previous work⁽²⁾ that binary alloys of most of these elements (including the major impurities in the present beryllium, Al, Si, Mg) with beryllium containing 1% of the added element revealed only minute differences in lattice constants from those of pure beryllium even after quenching from 1000°C. Furthermore, much of the Mg, which was the largest metal impurity in the beryllium, was undoubtedly distilled off during the stress anneal in vacuum given each specimen before using. Only copper (of the listed elements) was found to be appreciably soluble in solid beryllium, but it is present in the beryllium powder in sufficiently small amounts to be unimportant. The powder assayed only about 97% beryllium by weight indicating, according to the analysts, the presence of about 2% by weight of oxygen (for which no reliable direct method of analysis is yet available.) It is probable that a large part of this oxygen was picked up by the fine powder during ball milling, for experience has indicated that beryllium in finely divided form has a strong affinity for oxygen even at room temperature. However, here again previous work⁽²⁾ suggests that oxygen, too, has little effect on the lattice dimensions of beryllium.

The order of magnitude of the total influence of the impurities (perhaps excluding the oxygen) on the beryllium unit cell dimensions may be indicated by the following figures: In all the previous measurements made in these laboratories on the purest beryllium available, the a_0 parameter has been found to be 2.2808 to 2.2810 Å° at 25°C; the corresponding value for the powder, the analysis of which is given in Table II, is 2.2812₆ Å°.

 (2) "Preliminary Studies of the Physical Metallurgy of Beryllium", *P. Gordon*
 Report No. MDDC 137C.

Measurements of the lattice dimensions of beryllium have been made at temperatures in the range of 25° to 1000°C* on three separate specimens prepared from the Brush powder. The data obtained (listed in Table I of the Appendix) are plotted in the curves of Figures 6-9. Figures 6 and 7 show the variation of the a_0 and c_0 dimensions of the unit cell as a function of temperature, Figure 8 the resulting volume changes and Figure 9 the trend in the axial ratio, c/a .

From these data it is possible to calculate the linear and volume coefficients of thermal expansion for beryllium. This has been done and the results plotted in the curves of Figures 10 and 11 as a function of temperature. In Figure 10 are represented the true coefficients of expansion calculated from the slopes of the a_0 , c_0 and volume - versus temperature - curves respectively at any given temperature. Thus, the values given on the ordinate of the graph in Figure 10 are values of $\frac{1}{x} \frac{dx}{dT}$, where x is either the a_0 or c_0 dimension of the unit cell volume at the temperature, T . The slopes were found by drawing the best curves through the experimental data, picking values of, say, the a_0 parameter from the proper curve at points 50° above and 50° below the temperature in question, and dividing the difference between the two values thus obtained by the temperature difference, 100°C. The volume coefficients were calculated not only in this way, but also from the relationship

$$\alpha_v = 2\alpha_{\perp} + \alpha_{\parallel}$$

where α_v = volume coefficient of expansion

α_{\perp} = linear coefficient of expansion \perp to hexagonal axis

α_{\parallel} = linear coefficient of expansion \parallel to hexagonal axis

* The apparatus could be used at considerably higher temperatures by making a few minor changes in the materials used to build the furnace, particularly the transite faces.

Consequently, two sets of points, corresponding to the two methods of calculation, are shown on the volume curve in Figure 10. The good check of these two sets of values is an indication that the three basic curves in Figures 6, 7 and 8 have been consistently drawn through the experimental points.

These coefficient curves are, perhaps, of the greater scientific interest, but from the practical point of view the curves shown in Figure 11 should be more useful. Here are plotted the more generally used coefficients of thermal expansion α_{\perp} , $\alpha_{||}$ and α_v , as defined by the equations

$$(\text{length})_T = (\text{length})_{25} (1 + \alpha_{\perp} T) \quad \perp \text{ to the hexagonal axis}$$

$$(\text{length})_T = (\text{length})_{25} (1 + \alpha_{||} T) \quad || \text{ to the hexagonal axis}$$

$$(\text{volume})_T = (\text{volume})_{25} (1 + \alpha_v T)$$

Although the volume coefficients of expansion are applicable to beryllium specimens of any type, it should be remembered that the linear coefficients can be rigorously applied only to single crystals where the direction of the expansion with respect to the hexagonal axis is known. However, the values read from the curves may be used as very close approximations for extruded round rods of beryllium where the extrusion reduction in area was greater than about 6 or 8 to 1. It has been demonstrated⁽²⁾ that such material has a high degree of preferred orientation, the basal (0001) planes lying within about 6° or 7° of parallelism with the rod axis, but being randomly rotated about this axis. Thus, the longitudinal coefficient of thermal expansion for extruded rods is given very closely by the coefficient perpendicular to the hexagonal axis of the unit cell; the coefficient of radial thermal expansion for the rods is the arithmetical average of those \perp and $||$ to the hexagonal axis; that is $\frac{\alpha_{\perp} + \alpha_{||}}{2}$. For a polygrained specimen exhibiting no preferred orientation, the coefficient of linear thermal expansion in any direction may be taken as equal

to $\frac{2\alpha_{\perp} + \alpha_{\parallel}}{3}$.

The maximum relative error in the individual lattice constants plotted in Figures 6 to 9 is believed to be within $\pm 0.01\%$, the major part of this error being the result of temperature uncertainty which ranged from $\pm \frac{1}{2}^{\circ}\text{C}$ to $\pm 5^{\circ}\text{C}$ (see Appendix, Table I). These small errors in the parameters, however, lead to comparatively large errors in true coefficients of expansion which are based on the slope of the parameter-temperature curves. It is estimated that the calculated true coefficients are accurate to no better than $\pm 5\%$ at the extremities of the temperature range investigated, but are considerably less uncertain at the intermediate temperatures. The mean coefficients, on the other hand, are relatively inaccurate only at the lowest temperatures where the parameter change from 25°C to the temperature in question is small. The accuracy is probably about $\pm 5\%$ at these low temperatures, approaching ± 0.2 to 0.3% as the temperature nears 1000°C .

The high temperature X-ray measurements have served not only to determine the coefficients of thermal expansion of beryllium, but have also supplied evidence on the question of whether or not beryllium undergoes an allotropic transformation at some elevated temperature. Such a transformation in beryllium has been reported in the literature on several occasions. Lewis⁽³⁾ found indications of allotropic transformations at about -45°C and 450°C by thermal EMF and electrical resistivity measurements. Noyce and Daane⁽⁴⁾ reported a transformation at 730°C on the basis of thermal and dilatometric effects, both effects being very small.

(3) Lewis, E. J. Phys. Rev., 34, 1575, 1929

(4) Noyce, W. K. and Daane, A. H., Report #CT-2404

Attempts by Dr. A. R. Kaufmann and the present author to check the results of Noyce and Daane by careful thermal analysis gave no evidence of the alleged transformation⁽⁵⁾, however. In addition, Jaeger et al⁽⁶⁾⁽⁷⁾ reported a transformation in Be based on X-ray and specific heat measurements. They gave the structure of the high temperature phase as hexagonal close packed with a relatively large unit cell ($a_0 = 7.1\text{\AA}$, $c_0 = 10.8\text{\AA}$, 60 atoms per unit cell). Their X-ray measurements were made at room temperature, but they indicated that the high temperature phase was most successfully produced by heating to 630°C.

The present high temperature X-ray measurements give strong evidence against the occurrence of a phase transformation at any temperature between 25°C and 1000°C. In Figure 12 are reproduced several X-ray photographs taken at temperatures within this range. (The extraneous spotty lines in these pictures are due to the beryllium radiation shields between the specimen and the X-ray source. Since these spots were, in general, not superimposed on the lines from the specimen, they led to no measurement difficulties). In each case the specimen was generally at the indicated temperature for about 2 to 3 hours before the exposure was started (to allow stabilization of the temperature) and then from 2 to 4 hours more during the exposure. It seems highly probable that, in these periods of time at the higher temperatures the formation of a stable high temperature phase would be sufficiently far advanced to be detectable in the diffraction pattern. If such a transformation had in fact taken place, the diffraction patterns would be expected to reveal a new set of lines or a sudden large discontinuous shift in the lines as the temperature was

-
- (5) Gordon, P., and Kaufmann, A. R., MIT Progress Report Nov. 1945
 - (6) Jaeger, F. M., and Zanstra, J. E., Proc. Acad. Amst. 636, 36, 1933
 - (7) Jaeger, F. M. and Rosenbloom, E., Proc. Acad. Amst. 35, 1032, 1055; 57, 1934, 67; Rec. Trav. Chim. Pays-Bas, 53, 1934, 451

raised. Actually, as can be seen in Figure 12, the lines of the room temperature hexagonal close-packed beryllium phase persisted with essentially undiminished intensity at all temperatures up to 1000°C. They underwent a steady shift in position toward lower angles as the temperature was raised, consistent with a gradual increase in lattice parameter and a few new lines of higher indices appeared on the high angle portion of the film as the increasing temperature brought the $\sin^2 \theta$ values for these lines below unity. No sudden shift in line position was noted at any temperature, nor was there any evidence of a new set of lines corresponding to a high temperature phase. At 1000°C, however, there appeared on the film for all three specimens a faint alpha doublet and a very faint beta line, (see Figure 12) which were not present at any of the lower temperatures. It was immediately suspected that these were BeO lines resulting from the formation of an oxide film on the surface of the beryllium specimens. That this was actually the case was conclusively proven by making a diffraction pattern of pure BeO at 1000°C using Fe and Co radiation. The position of the strongest alpha doublet and the strongest beta line appearing on the BeO pattern thus obtained checked exactly with those of the corresponding lines on the 1000°C beryllium film.

As has been indicated, the metal powder used in the above experiments assayed only about 97% beryllium. There remained, thus, a small probability that the presence of the impurities (largely oxygen) may have inhibited the formation of a high temperature phase which would normally be present in purer beryllium. Fortunately, some much higher assay beryllium powder recently became available. This powder was ground from vacuum cast beryllium by special techniques devised at Brush Beryllium Company with the specific purpose of preventing the contamination of the powder by oxygen. The quantities of impurities present in the powder are indicated

in Table III. Since the metal assayed 99.4% Be and the total impurity content (largely Al, Fe, Si and C) approximated 0.7%, it may be seen that the powder was essentially free of oxygen.

Table III.

Analysis of the 99.4% Assay Beryllium Powder

| Element | Wgt. % | Atomic % |
|----------|--------|----------|
| Be Assay | 99.4 | |
| C | 0.12 | 0.091 |
| Al | 0.17 | 0.057 |
| Ca | 0.014 | 0.0032 |
| Cr | 0.014 | 0.0024 |
| Cu | 0.010 | 0.0014 |
| Fe | 0.20 | 0.033 |
| Mg | 0.083 | 0.0031 |
| Mn | 0.020 | 0.0035 |
| Ni | <0.010 | 0.0016 |
| Si | 0.11 | 0.036 |

An X-ray specimen was prepared from this powder as received (-325 mesh) taking care to isolate the powder from contact with air as much as possible until it had been pressed into pellet form by the techniques described earlier. After a 600°C stress relief anneal in vacuum, X-ray photograms were made at 650°C and 900°C. In neither case was there any indication of the formation of a high temperature phase.

It is considered that these experiments provide persuasive evidence that the hexagonal close-packed form of beryllium encountered at room temperature is stable up to at least 1000°C.

ACKNOWLEDGEMENTS

The writer wishes to express his sincere thanks to Dr. A. R. Kaufmann for his continued helpful interest and to Herbert Sawyer whose assistance in the laboratory was invaluable.

Appendix

Table I

Measured Lattice Constants

| Specimen | Temperature °C | | a ₀ , in k X U | c ₀ , in k X U | c ₀ /a ₀ | Unit Cell Volume (k X U) ³ |
|----------|----------------|-------------|------------------------------|------------------------------|--------------------------------|--|
| | Ave. | Uncertainty | | | | |
| R | 24 | ± 1/2 | 2.28126 | 3.57705 | 1.56802 | 16.1215 |
| P | 25 | ± 1/2 | 2.28126 | 3.57708 | 1.56803 | 16.1217 |
| I | 26 1/2 | ± 1/2 | 2.28127 | 3.57713 | 1.56804 | 16.1220 |
| R | 74 | ± 1/2 | 2.28253 | 3.57880 | 1.56791 | 16.1474 |
| P | 95 | 1 1/2 | 2.28295 | 3.57936 | 1.56787 | 16.1558 |
| R | 147 | 2 | 2.28547 | 3.58182 | 1.56721 | 16.2026 |
| P | 215 | 1 | 2.28771 | 3.58459 | 1.56689 | 16.2469 |
| I | 239 | 2 1/2 | 2.28862 | 3.58573 | 1.56678 | 16.2652 |
| R | 293 | 3 | 2.29117 | 3.58874 | 1.56634 | 16.3149 |
| P | 360 | 1 1/2 | 2.29361 | 3.59217 | 1.56616 | 16.3653 |
| R | 385 | 2 | 2.29489 | 3.59373 | 1.56597 | 16.3908 |
| I | 423 | 1 1/2 | 2.29624 | 3.59553 | 1.56583 | 16.4184 |
| P | 496 | 1 | 2.29973 | 3.59951 | 1.56519 | 16.4865 |
| I | 567 1/2 | 2 1/2 | 2.30320 | 3.60330 | 1.56448 | 16.5511 |
| P | 601 1/2 | 2 1/2 | 2.30445 | 3.60543 | 1.56455 | 16.5815 |
| I | 635 | 3 1/2 | 2.30941 | 3.61176 | 1.56393 | 16.6822 |
| P | 716 | 3 1/2 | 2.31022 | 3.61263 | 1.56376 | 16.6978 |
| P | 793 1/2 | 3 | 2.31426 | 3.61783 | 1.56328 | 16.7804 |
| I | 807 1/2 | 2 1/2 | 2.31471 | 3.61824 | 1.56315 | 16.7889 |
| P | 895 | 3 1/2 | 2.31941 | 3.62476 | 1.56279 | 16.8874 |
| I | 901 1/2 | 3 | 2.31950 | 3.62474 | 1.56273 | 16.8887 |
| R | 904 1/2 | 3 1/2 | 2.32022 | 3.62544 | 1.56254 | 16.9025 |
| R | 989 1/2 | 4 1/2 | 2.32514 | 3.63237 | 1.56222 | 17.0066 |
| P | 1004 | 5 | 2.32538 | 3.63243 | 1.56208 | 17.0104 |
| I | 1013 | 3 1/2 | 2.32557 | 3.63214 | 1.56196 | 17.0089 |

AppendixTable II

True Coefficients of Thermal Expansion: $\alpha = \frac{1}{x} \frac{dx}{dT} \times 10^6$ as Calculated
from Figures 5, 6 and 7

α_{\perp} = Coefficient perpendicular to hexagonal axis

α_{\parallel} = Coefficient parallel to hexagonal axis

α_v = Volume coefficient

| Temperature °C | α_{\perp} | α_{\parallel} | α_v | |
|----------------|------------------|----------------------|------------------|--|
| | | | From Figure 7 | $2\alpha_{\perp} + \alpha_{\parallel}$ |
| 50 | 11.7 | 9.4 | 29.8 | 32.9 |
| 75 | 13.3 | 10.0 | 35.3 | 36.5 |
| 100 | 14.7 | 10.8 | 39.9 | 40.2 |
| 150 | 16.2 | 12.1 | 45.1 | 44.6 |
| 200 | 16.7 | 13.1 | 47.4 | 46.5 |
| 250 | 17.4 | 13.9 | 49.2 | 48.8 |
| 300 | 18.2 | 14.4 | 50.3 | 50.8 |
| 350 | 18.5 | 14.5 | 52.0 | 51.6 |
| 400 | 19.1 | 14.9 | 53.0 | 53.1 |
| 450 | 19.6 | 15.2 | 54.1 | 54.4 |
| 500 | 20.1 | 15.6 | 55.8 | 55.9 |
| 550 | 20.4 | 16.2 | 58.0 | 57.0 |
| 600 | 20.6 | 16.5 | 58.5 | 57.7 |
| 650 | 21.0 | 16.9 | 59.5 | 58.9 |
| 700 | 21.4 | 17.4 | 60.6 | 60.1 |
| 750 | 21.6 | 17.8 | 61.0 | 61.1 |
| 800 | 22.0 | 18.3 | 61.9 | 62.3 |
| 850 | 22.4 | 19.0 | 63.2 | 63.9 |
| 900 | 23.2 | 19.6 | 65.7 | 65.9 |
| 950 | 23.6 | 19.8 | 67.0 | 67.1 |

Appendix

Table III

Mean Coefficients of Thermal Expansion: $\alpha = \frac{x_T - x_{25}}{x_{25}(T-25)} \times 10^6$

as Calculated from Figures 5, 6 and 7

α_{\perp} = Coefficient perpendicular to hexagonal axis

α_{\parallel} = Coefficient parallel to hexagonal axis

α_v = Volume coefficient

| Temperature °C | α_{\perp} | α_{\parallel} | α_v |
|----------------|------------------|----------------------|------------|
| 50 | 10.7 | 8.7 | 26.0 |
| 75 | 11.7 | 9.4 | 28.5 |
| 100 | 12.6 | 9.6 | 32.0 |
| 150 | 13.9 | 10.4 | 37.0 |
| 200 | 14.7 | 11.0 | 39.5 |
| 250 | 15.1 | 11.6 | 41.6 |
| 300 | 15.7 | 12.1 | 43.0 |
| 350 | 16.1 | 12.5 | 44.4 |
| 400 | 16.5 | 12.8 | 45.5 |
| 450 | 16.8 | 13.1 | 46.5 |
| 500 | 17.2 | 13.3 | 47.4 |
| 550 | 17.5 | 13.6 | 48.6 |
| 600 | 17.8 | 13.8 | 49.5 |
| 650 | 18.0 | 14.1 | 50.2 |
| 700 | 18.3 | 14.3 | 51.2 |
| 750 | 18.5 | 14.5 | 52.0 |
| 800 | 18.7 | 14.8 | 52.7 |
| 850 | 19.0 | 15.0 | 53.4 |
| 900 | 19.2 | 15.3 | 54.2 |
| 950 | 19.5 | 15.5 | 55.0 |
| 1000 | 19.7 | 15.8 | 55.8 |

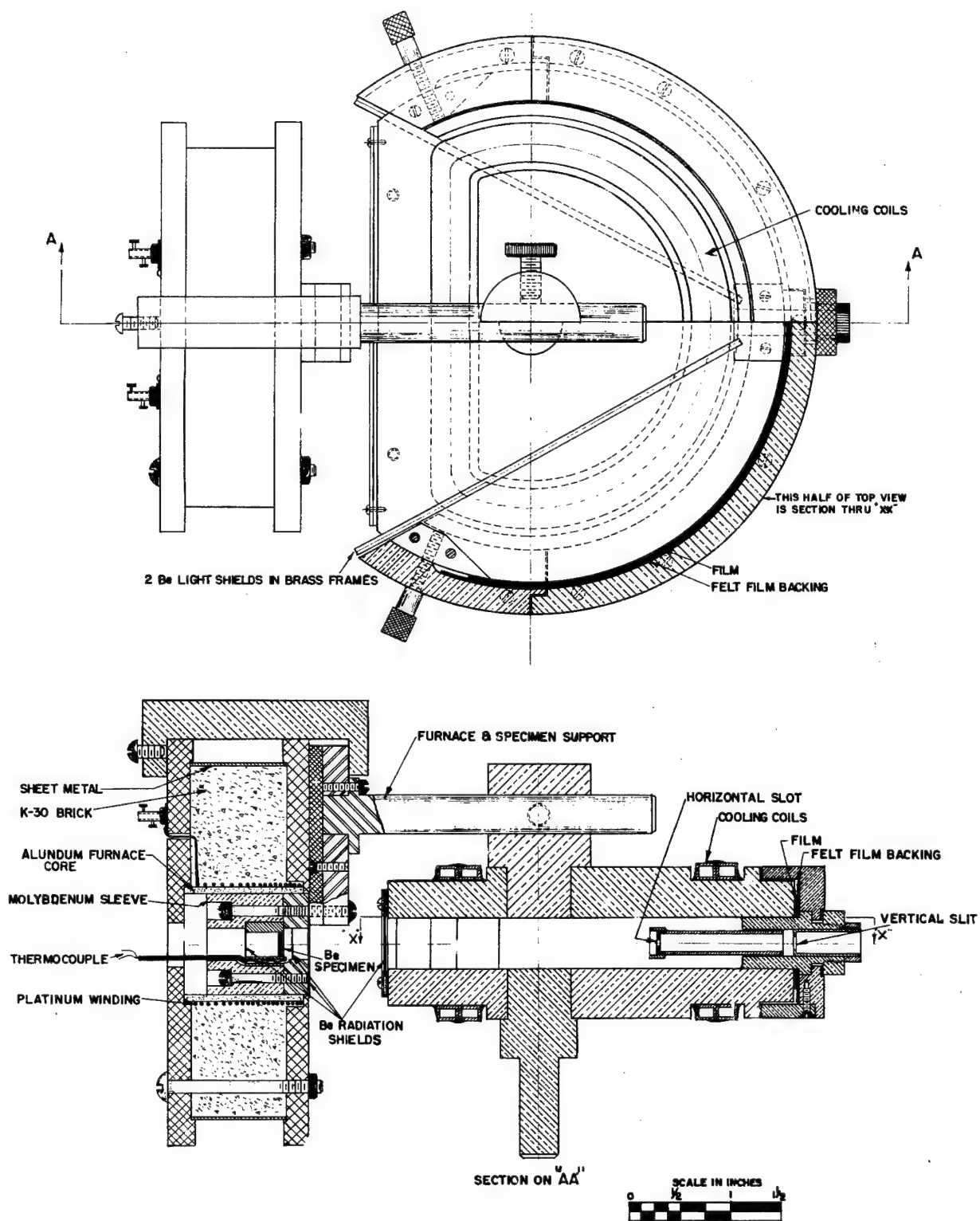


Figure 1. Schematic drawing of the high temperature precision X-ray camera.

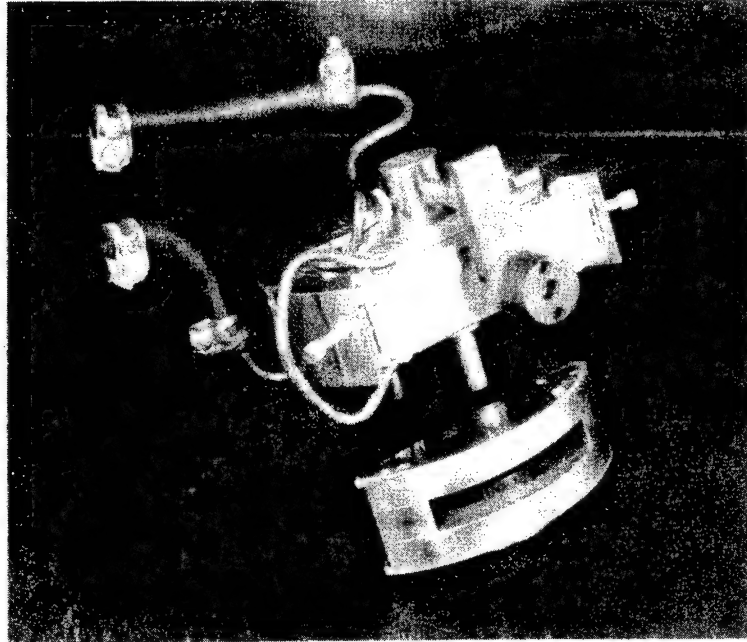


Figure 2. View of the camera with high temperature attachments in place, but showing the removed rear segment which may be replaced for room temperature measurements.

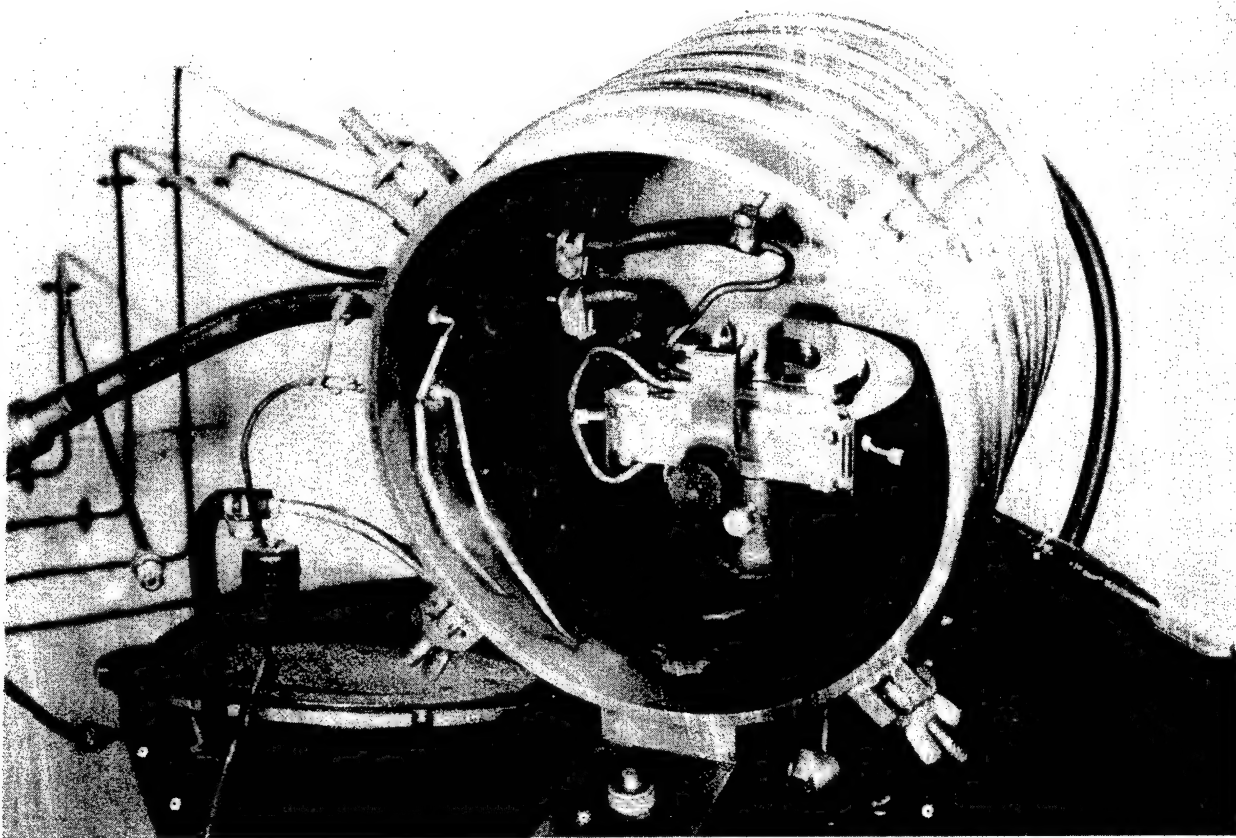


Figure 3. View of the camera in place in the vacuum chamber, but with the furnace removed.

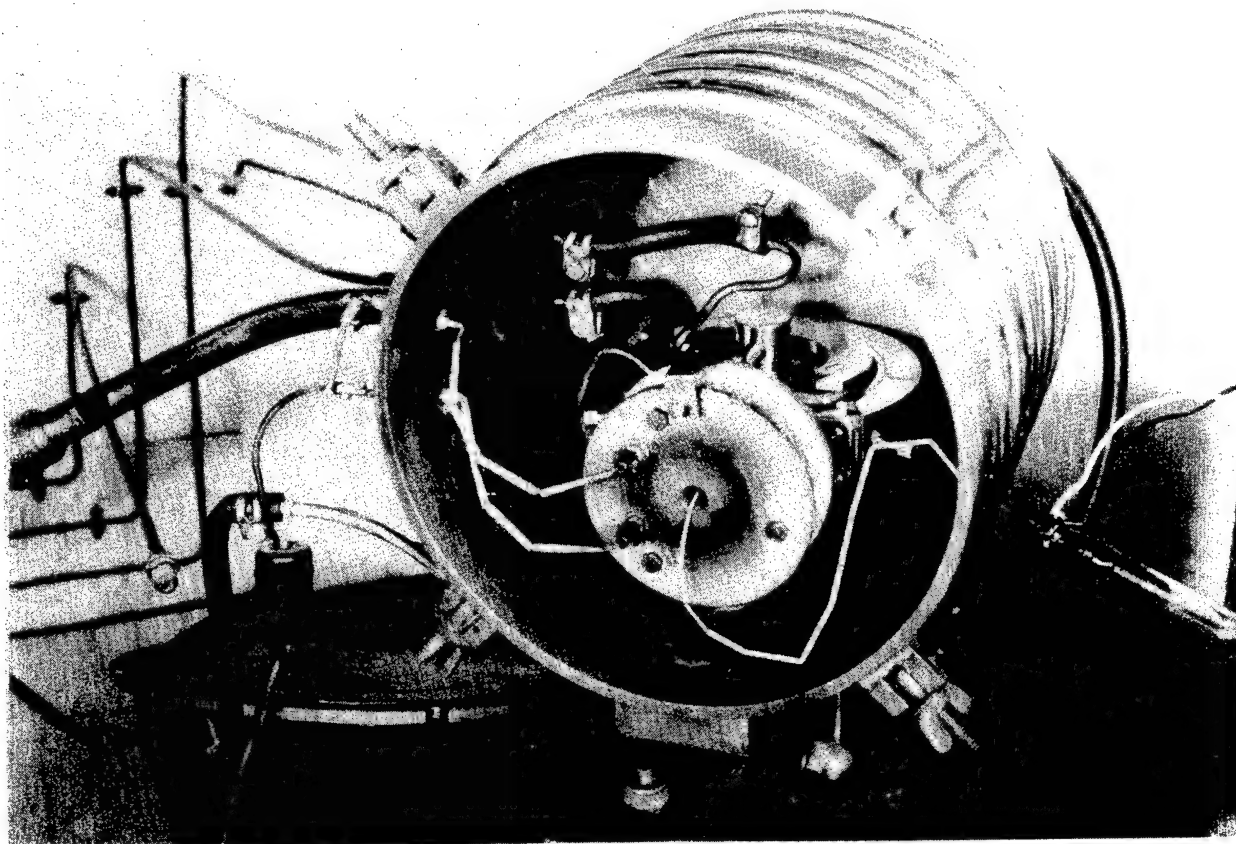


Figure 4. View of the camera and furnace
in place in the vacuum chamber.

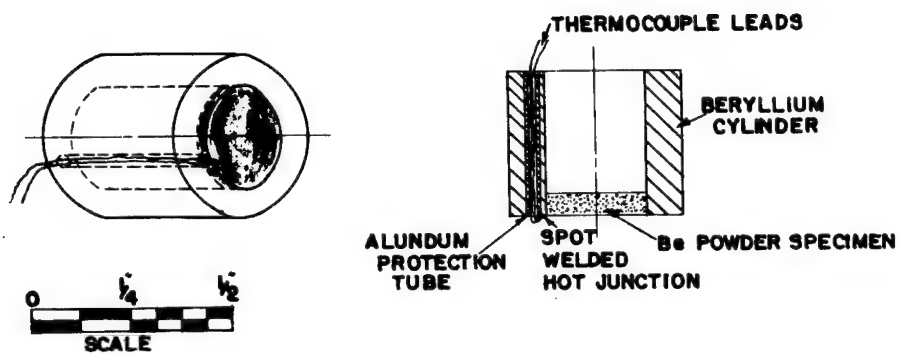


Figure 5. Sketch of the specimen and specimen holder indicating method of attaching thermocouple.

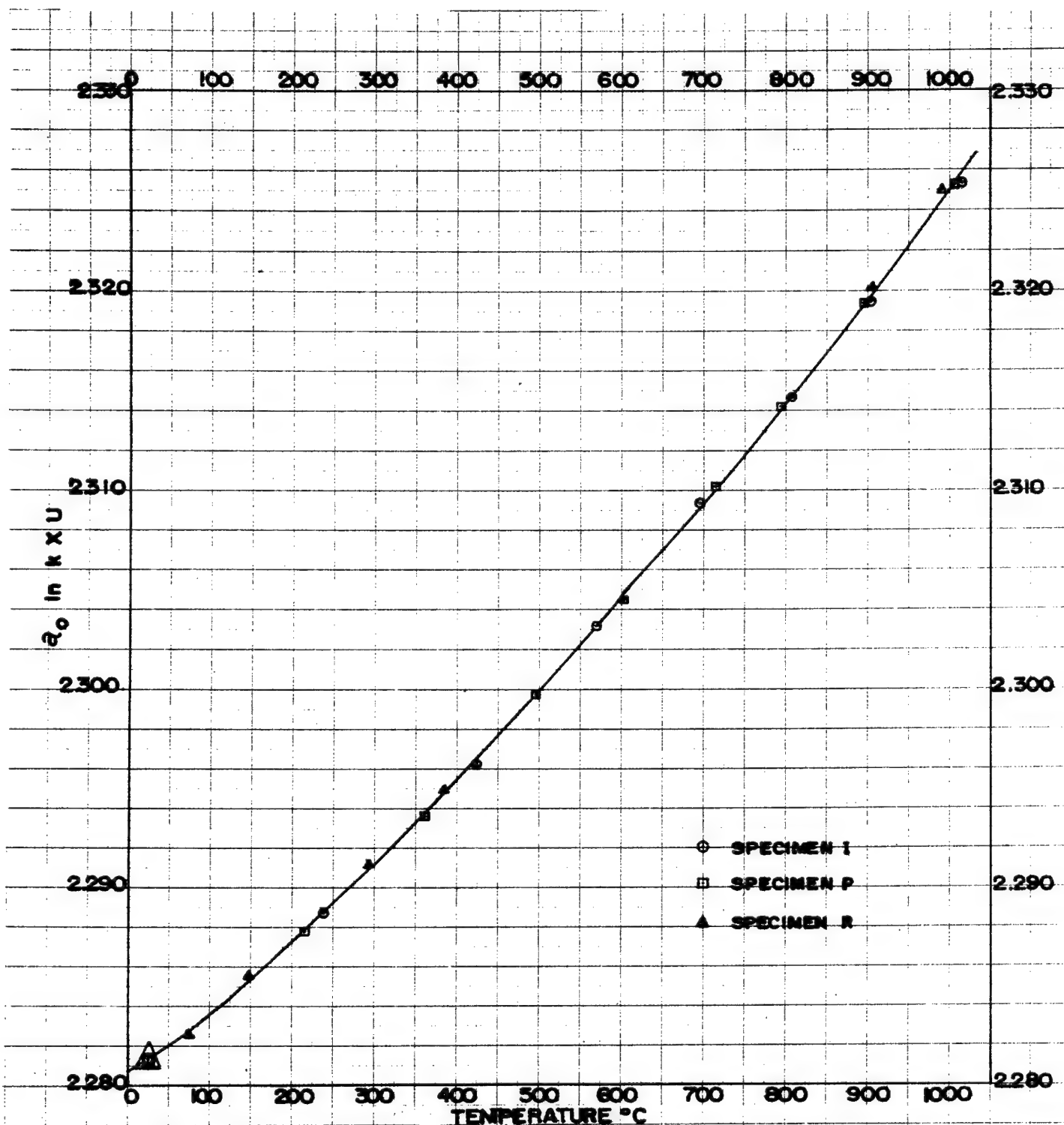


FIG. 6 CHANGE IN THE a_0 PARAMETER (EDGE OF CELL PERPENDICULAR TO HEXAGONAL AXIS) OF B_{10} AS A FUNCTION OF TEMPERATURE.

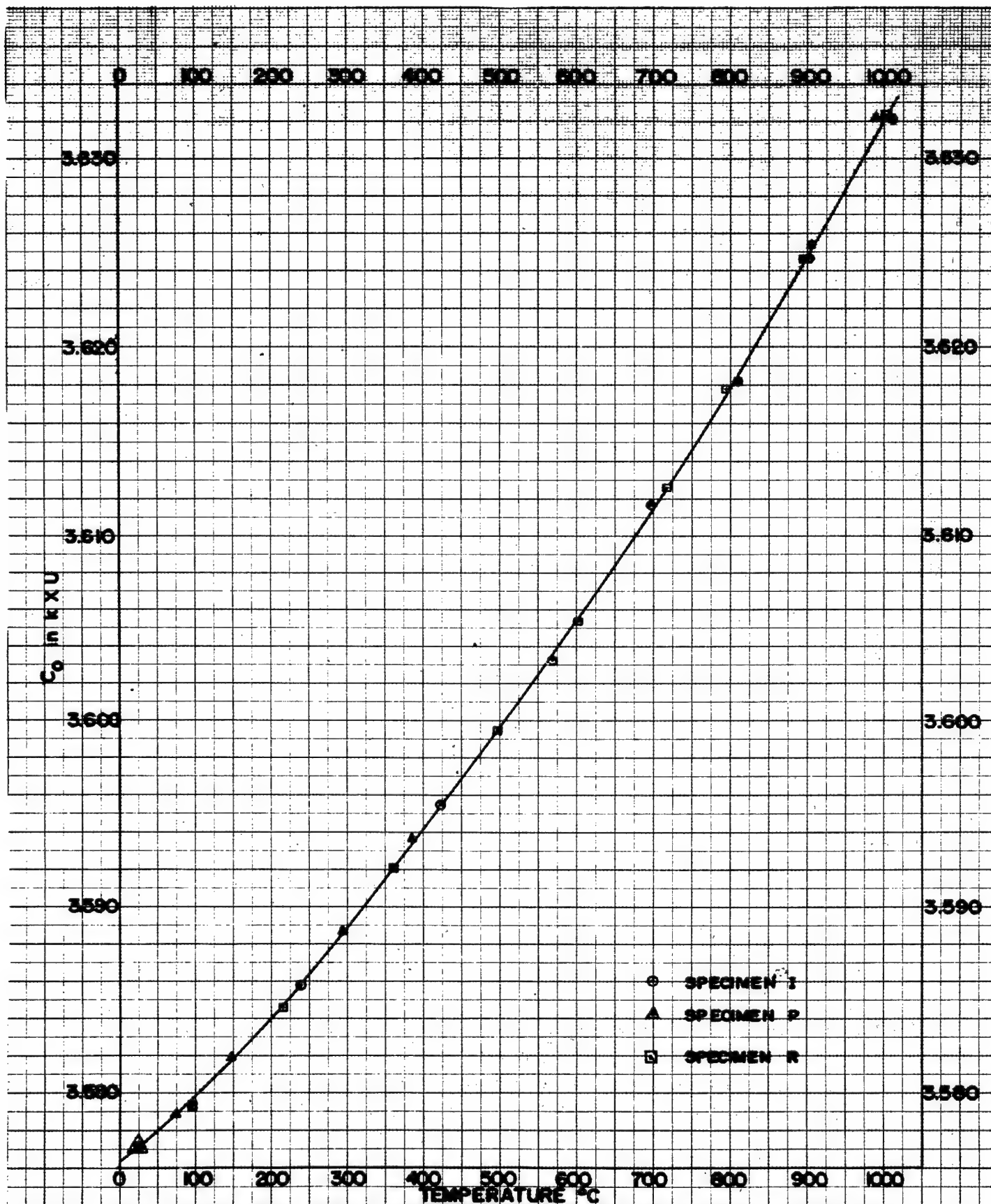


FIG. 7 CHANGE IN THE C_0 PARAMETER (LENGTH OF THE HEXAGONAL AXIS) OF B_2 AS A FUNCTION OF TEMPERATURE

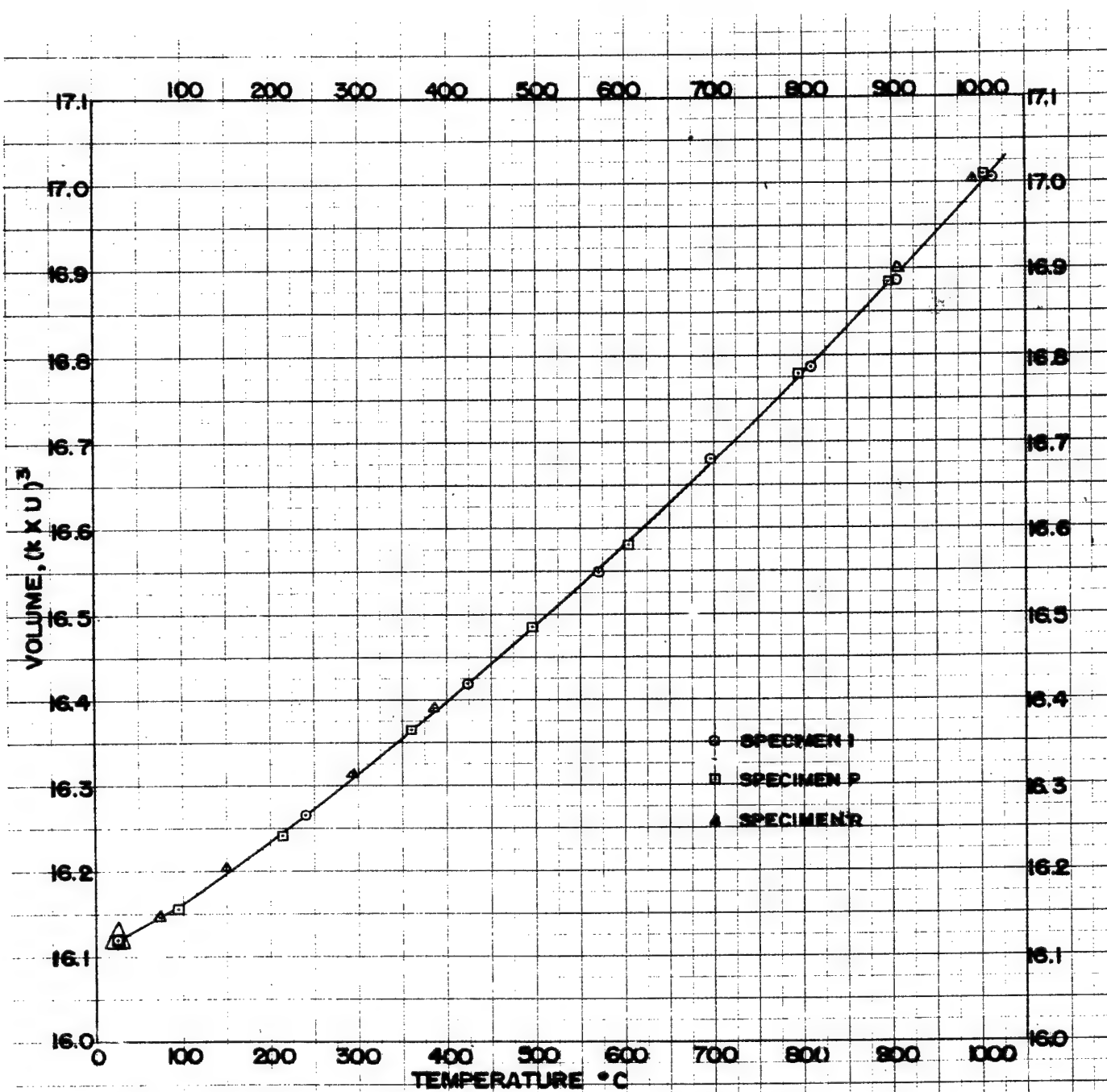


FIG. 8 CHANGE IN VOLUME OF THE B₂ UNIT CELL AS A FUNCTION OF TEMPERATURE.

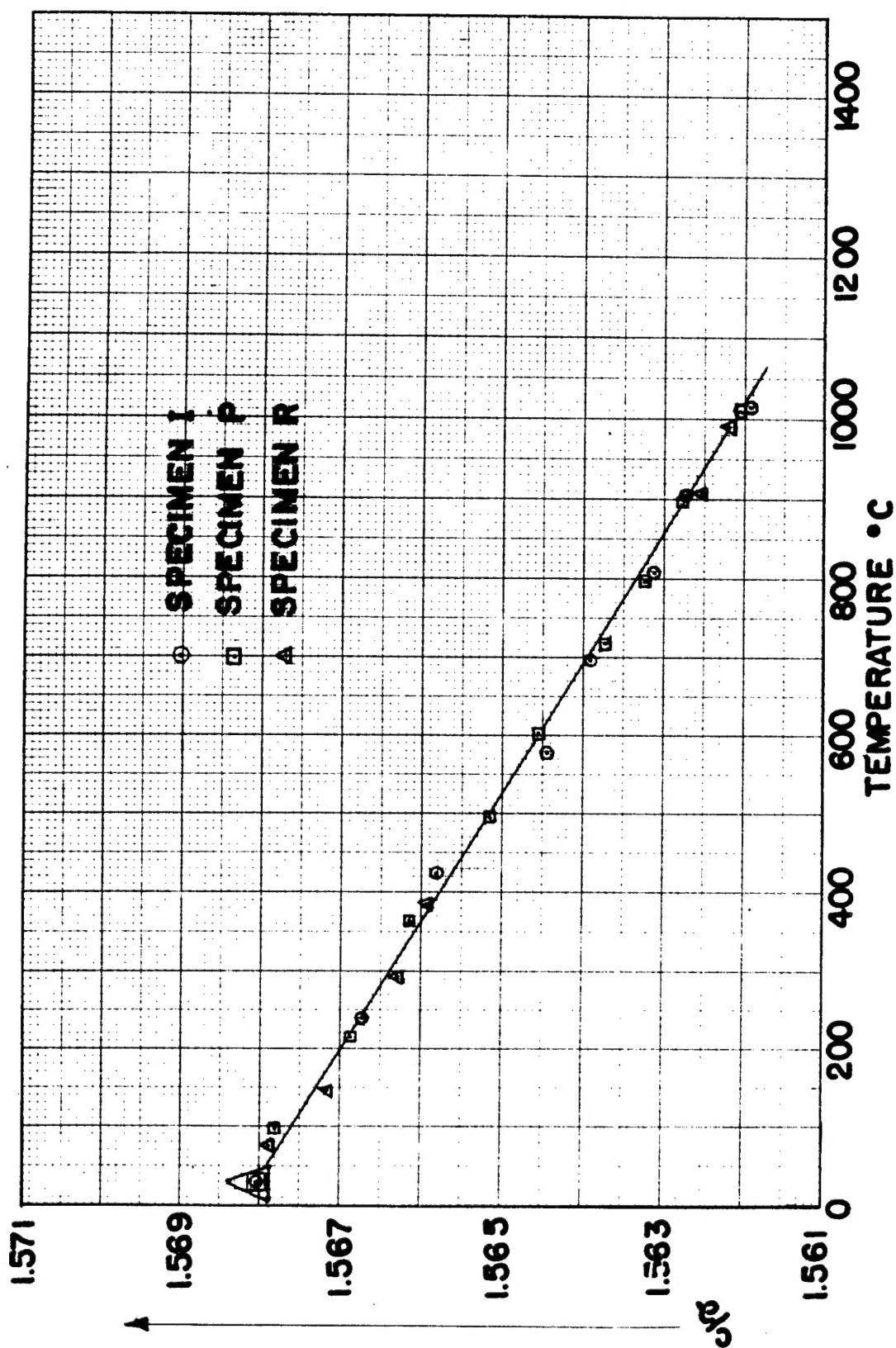


FIG. 9 AXIAL RATIO, c/a , OF BERYLLIUM AS A FUNCTION OF TEMPERATURE

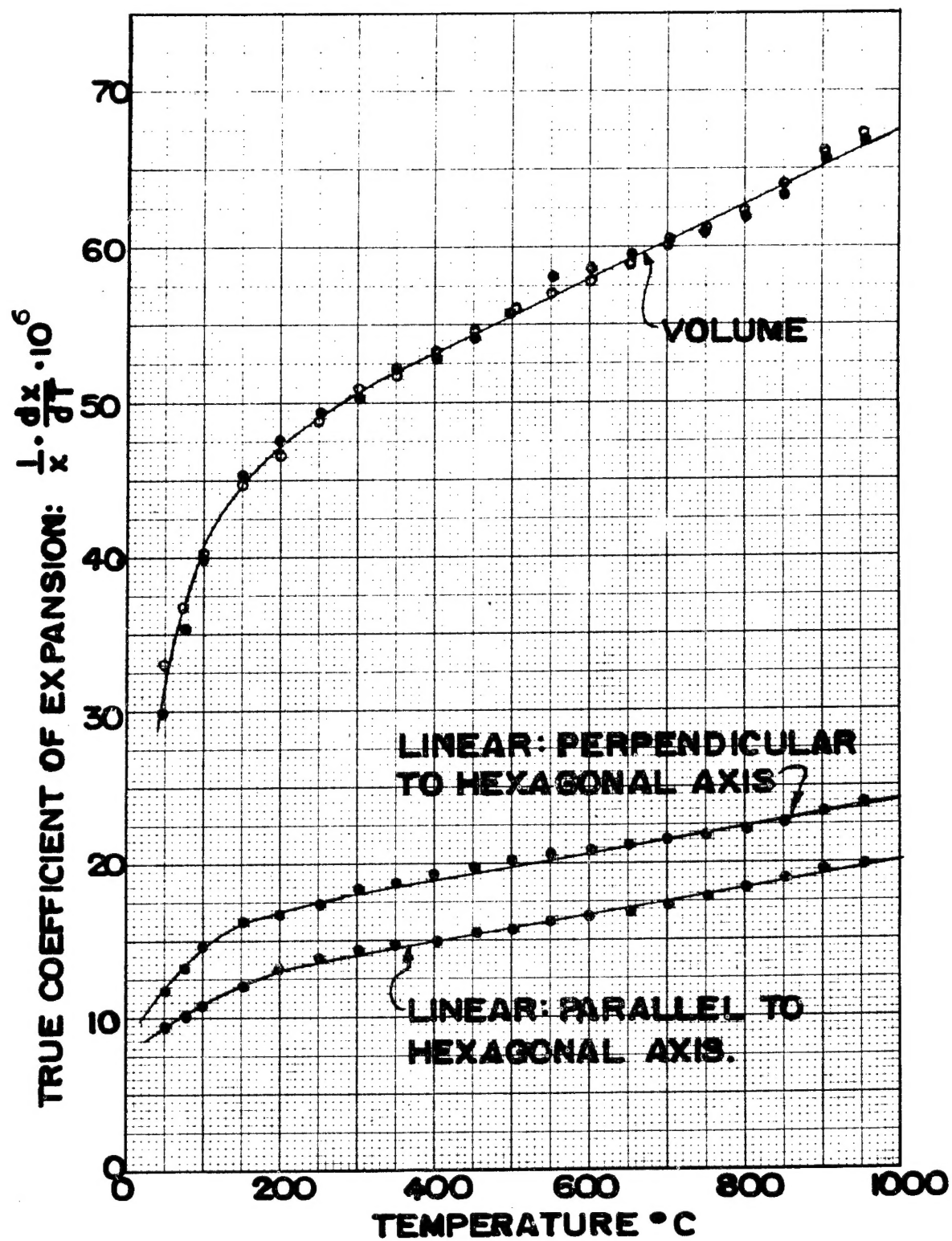


FIG. 10 TRUE COEFFICIENTS OF THERMAL EXPANSION OF BERYLLIUM

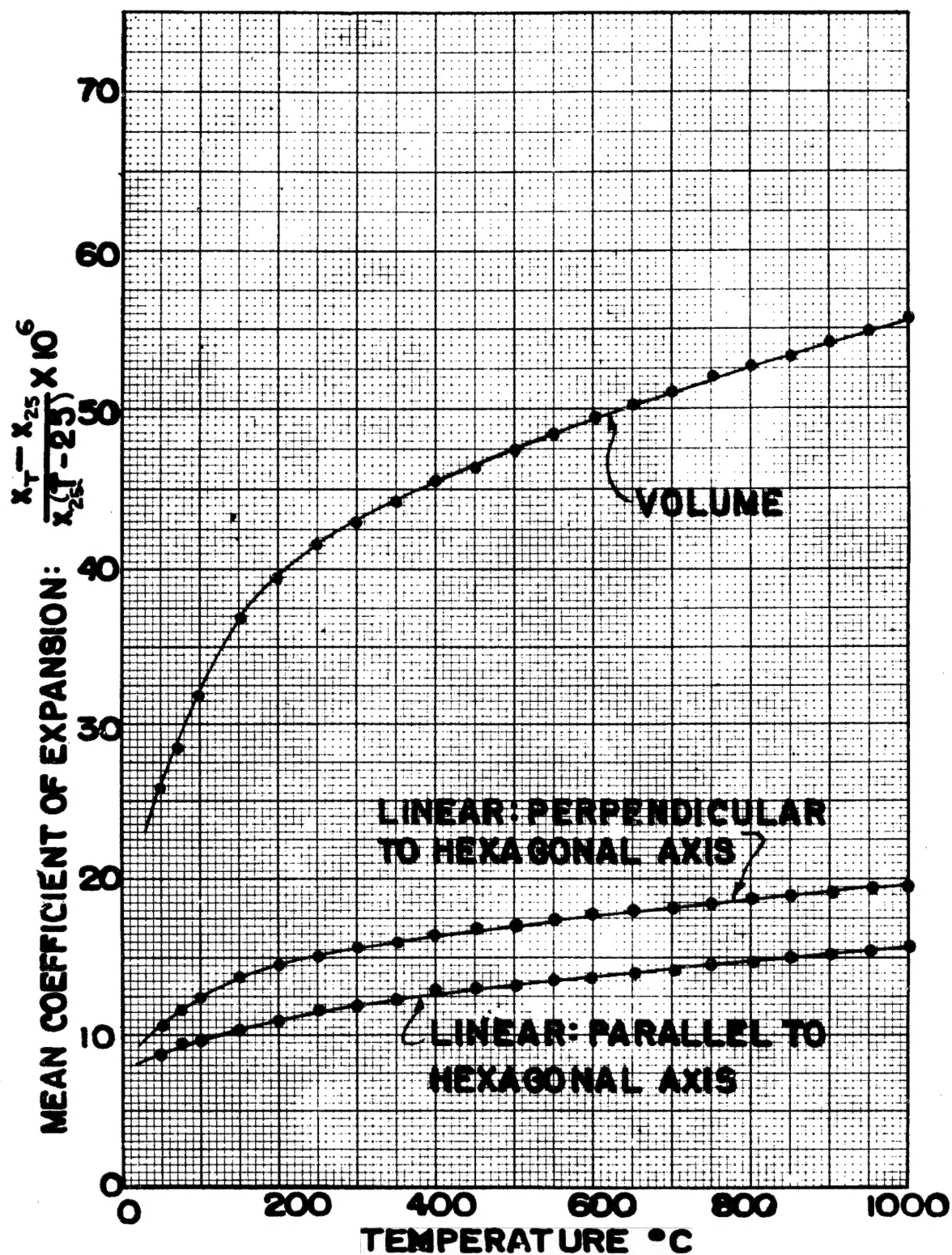


FIG. II MEAN COEFFICIENTS OF THERMAL EXPANSION OF BERYLLIUM

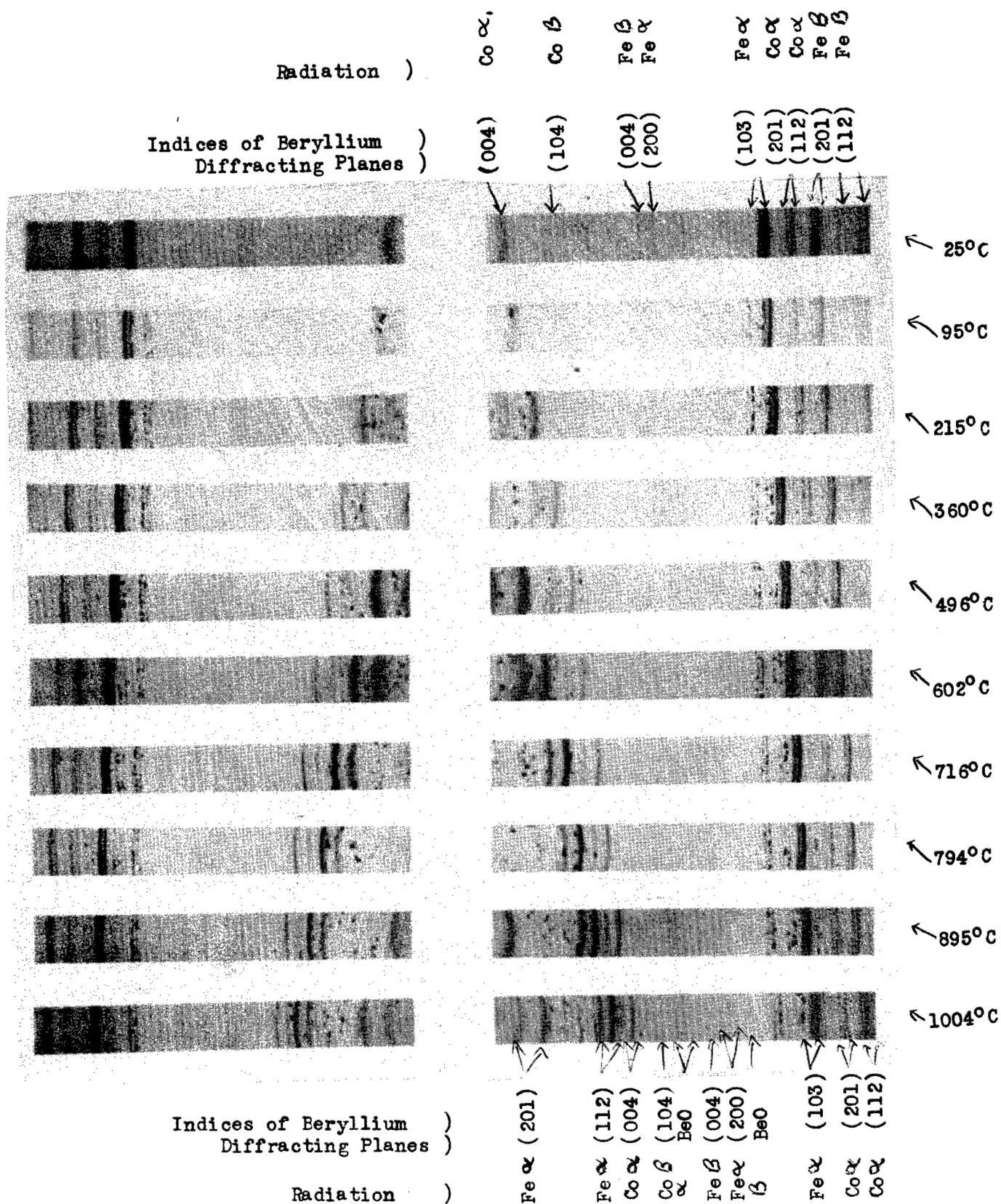


Figure 12. Variation of the back reflection powder diffraction pattern of beryllium as a function of temperature.